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## (54) POWDERED COATING COMPOSITIONS

(71) We, CABOT CORPORATION, of 125, High Street, Boston, Massachusetts, United States of America, a Corporation organised and existing under the Laws of the State of Delaware, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to powdered coating compositions containing high-molecular weight synthetic organic resins in particulate solid form. The solid resins to which the invention relates include any thermoplastic or thermosetting polymers which can be reduced to solid particles below 500 microns in size.

Recently, commercial success has been achieved in applying resinous coatings to various articles by solventless techniques. These so-called "powder coating" techniques include a variety of methods of applying finely powdered solids to the surfaces to be coated, such as electrostatic deposition of gas-projected streams of particles and dynamic immersion of a normally preheated object into a fluidized powder bed.

With the advent of such new methods of coating objects by applying powdered resinous compositions, several problems peculiar to the nature of finely subdivided resin solids have arisen which threaten the successful execution of such operations. Most of these difficulties seems to revolve about the often eccentric and unpredictable flow behaviour of the various powdered resins which may exhibit itself in the preliminary bulk handling stages as well as in the most critical final application step. For example, it is extremely difficult to produce coatings of uniform and reproducible thickness if the electrical characteristics of the resin particles vary during the use of electrostatic methods and/or if the solids concen-

tration in the fluidized bed varies excessively due to channelling or irregular bubbling of the fluidized gas flowing therethrough. 45

According to the present invention, there is provided a powdered coating composition comprising a synthetic organic resinous particulate solid below 500 microns in particle size and at least 0.1% by weight thereof of hydrophobic pyrogenic silica below 50 millimicrons in particle size. 50

Preferably the finely divided synthetic resinous particles should have a particle size of below 500 microns and above 1 micron and have as a major component a film-forming synthetic organic polymer and between 0.1% and 25% by weight of separate particles of finely divided hydrophobic pyrogenic silica having an average particle size below 50 millimicrons and preferably below 20 millimicrons. Most preferably the surface of the silica should be rendered hydrophobic by chemically attaching organosilicon groups thereon. Suitably such organosilicon groups may conform to the general formula: 55 60 65



where Si is silicon, each R is any alkyl, aryl, alkaryl, alkoxy, aryloxy, alkaryloxy, or aralkoxy radical; a is 2 or 3; each X is a halogen or hydroxyl radical; b is 0 to 1; and the sum of a+b is 3. 70

In the most preferred groups, a is 3 and "X" radicals are not present. 75

In order to ensure the attainment of finished coatings having superhydrophobic or waterproof character, the amount of said hydrophobic pyrogenic silica blended with the said resinous particles should be over 1% by weight based upon the weight of said resinous particles. The minimum amount of said hydrophobic pyrogenic silica required to attain a super-hydrophobic finished coating will depend 80

upon several factors including the particle size of resinous powder and the degree to which it fuses and flows during the process of applying and bonding the coating to the article being coated. However, the most important consideration in this connection is the fineness of the pyrogenic silica particles themselves. For those silicas within the preferred particle size range, i.e. averaging less than 20 millimicrons, mixtures containing between 2 and 10 parts by weight of silica and between 98 and 90 parts by weight of resinous powder will generally produce excellent super-hydrophobic finished coatings whereas for the coarser silicas, i.e. those between 25 and 50 millimicrons in average particle size, the most useful mixtures will usually contain between 5 and 20 parts by weight of hydrophobic silica and between 95 and 80 parts by weight of resinous powder.

As already indicated, the resinous powders can be derived from almost any type of synthetic organic polymer provided that they are available in particle sizes below 500 microns. The preferred powder resin particles for most applications will generally have a mean particle size somewhere between 10 and 250 microns. Likewise, it has been indicated that both thermoplastic and thermosetting resins can be used and, in fact, the chemical nature of the polymeric resin component thereof is not usually critical or of primary concern. However, the classes or resins to which the invention is primarily applicable, include epoxy resins, vinyl resins, nylons, polyesters, polymers and copolymers of various  $\alpha$ -monoolefinic hydrocarbons such as ethylene, propylene and butylenes, as well as various inter-polymers and modified forms of these more basic types including such variations as chlorinated, carboxylated, sulfonated, and grafted substitutions.

It should also be made clear that the powdered resinous particles referred to herein are seldom composed solely of pure polymeric resin. Usually, said particles are composed of resinous compounds which already include various additives such as antioxidants, catalysts or curing agents, pigments, fillers, flow-control agents and the like. However, in most cases, such additives are used in relatively minor amounts so that the major part of said resinous powders is generally composed of synthetic organic polymeric resins of one kind or another.

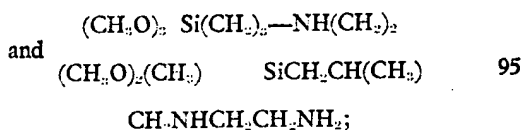
To insure good performance, in the present invention, the pyrogenic silica should possess a BET surface area of at least 100 square meters per gram, and preferably at least 150 square meters per gram. The art of treating such pyrogenic silicas with organo compounds reactive with hydroxyl groups (or silanol groups) on the surface of the silica, to render same hydrophobic is by now well developed. For example, reference is made to such patent

literature as United States Patents 2,993,809, 3,024,126 and 3,393,155. Accordingly, suffice it to say, that the surfaces of the silica can readily be reacted at moderate temperatures and/or pressures with various organo compounds, particularly organosilicon compounds such as organohalosilanes and the like so as to cover said surfaces with hydrophobic components, the preferred active groups in which probably conform to the generic formula,

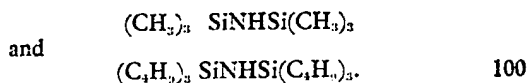


as defined previously herein. Said active hydrophobic groups are usually attached to the solid silica surface by regular covalent-type bonds, normally from the silicon atom to an oxygen atom on the silica particle. However, in some cases a form of hydrogen atom attached to the silicon atom and hydroxyl groups or the like on the surface of the silica particles.

Specific examples of organosilicon compounds which are often reacted with pyrogenic silicas to form surface structures like those described above are: organohalosilanes such as  $(\text{CH}_3)_3\text{SiCl}_2$ ,  $(\text{CH}_3)_2\text{SiBr}_2$ ,  $(\text{CH}_3)_2\text{SiCl}_2$  and  $(\text{C}_2\text{H}_5)_3\text{SiCl}$ ; organosilylamines such as



organodisilazanes such as



In most cases, the surface treatments must be sufficient to attach organo groups totalling at least 0.5% and preferably at least 1% by weight based on the dry weight of the silica particles treated. In many cases, especially with the most preferred higher surface area silicas, the concentration of organo groups thereon will equal 2% or more by weight.

The particle size range of the resinous-powder component will usually be selected in accordance with the method of application to be used in forming the finished coating. For example, a finer resinous powder may be desirable in electrostatic-gun projection methods than in fluidized-bed immersion techniques. Thus, typical resinous powders used in electrostatic spraying have particle sizes in the range from 5 to 100 microns whereas typical resinous powders used in fluidized-bed techniques might comprise various cuts in the range from 40 to 400 microns in particle size.

In any case, in forming the coating compositions of the present invention, suitable

mixtures of the very fine hydrophobic pyrogenic silica and the considerably coarser resinous powder can easily be prepared using only ordinary techniques of dry blending powders. Thus, the very fine silica particles seem to naturally cling to the surfaces of the resinous powder so that intimate mixtures are readily obtained and reparation, settling and segregation are not serious problems. Once the resin, or resinous compound, has been reduced to the particle-size range desired, the desired amount of hydrophobic pyrogenic silica can merely be added thereto and the mixture simply tumbled or otherwise agitated together, e.g. in a horizontal rotating barrel or drum or a vibratory container. More elaborate mixing equipment such as double-cone mixers, twin-shell blenders and the like, can, of course, be used if desired but are not usually required to achieve a suitable mixture of the essential powder components.

Other than the two essential powder components already discussed hereinabove, additional solid components can also be included, if desired, provided that they are in a suitable state of subdivision, i.e., usually similar to that of the resinous powder itself. Any liquid components to be included are preferably preincorporated in the resinous material before it is reduced to its final state of subdivision. However, components which are in liquid form can be added during the dry blending of the resinous powder and the fine silica component provided they are added very slowly and represent a very minor proportion (usually less than 1% by weight) of the total coating composition. Of course, the dry blending step should always be conducted at a temperature sufficiently low that the resinous powder does not tend to soften or become tacky.

The following specific examples illustrate several different embodiments of the present invention in the form of various coating compositions prepared in accordance therewith and show some of the typical advantages obtained therefrom.

#### EXAMPLE I

A powdered thermoplastic copolymer of propylene and maleic anhydride sold under the trade name HERCOPRIME PA 673 by Hercules Powder Company and having a melting temperature of approximately 155°C was sieved to obtain a fraction having a relatively narrow particle-size range largely between 5 and 60 microns. This material was used in a small fluidized bed powder coating using nitrogen gas fed under suitable pressure through sintered porous plate distributor at the bottom of the bed. Small metal objects preheated to 225°C. and immersed within the upper part of this fluidized bed for 15 seconds were satisfactorily coated with fused resin over all exposed surfaces. However, various instabilities such as channeling, slugging and

geysering, were noted from time to time in the fluidized bed which led to some irregularities and variations in thickness of the coatings on certain areas of the metal parts.

A batch of the same 5 to 60 micron fraction of HERCOPRIME PA 673 resin was dry blended with 0.4% of its weight of a highly hydrophobic pyrogenic silica having a mean particle size of 10 millimicrons and a surface area of just over 200 square meters per gram. The hydrophobicity of this silane-treated silica is of such a high degree that it floats dry and unwetted when placed in a pool of liquid containing a mixture of 17% isopropyl alcohol and 83% water by weight.

The resulting mixture was then used to coat similar metal objects in the same fluidized-bed apparatus with strikingly improved results. Thus, in this case, the bed fluidization action was much smoother and more regular with little or no channeling or lugging. Furthermore, the coatings deposited on the metal parts were more regular and uniform in thickness.

Substantially the same results were obtained when the proportion of hydrophobic pyrogenic silica added to the above resinous powder was varied between 0.1 and 1.0% by weight. Most surprisingly also, the bulk volumes of the mixtures containing such fractions of a per cent of said hydrophobic pyrogenic silica were 20 to 30% less than that of the original HERCOPRIME PA 673 resin and yet said mixtures showed no tendency to cake, plug or hang up during storage or bulk handling and, in fact, were actually easier to transfer and handle in routine operations generally.

Similar results were obtained when the same silica was added in amounts of 1% or less to other powdered resins including thermosetting resins such as epoxy resins.

#### EXAMPLE 2

A completely formulated, heat-curable epoxy resin blend powder sold under the trade name VIBRO-FLO Epoxy Powder E7100-1 by Armstrong Products Company was used as the resinous powder in this example. This powder was of rather narrow size distribution with an average particle size of approximately 50 microns and it already contained not only the reactive base epoxide resins but also the necessary curing agents and finely divided silica flow-control agents and the like already pre-compounded together.

This resinous powder was applied by means of an electrostatic gun at a rate of 25 milligrams per square inch to the surfaces of an earthed 4"×8" Q panel. The coated panel was then cured in an air-circulating oven at 200°C. for three minutes.

A mixture of 96 parts of the same VIBRO-FLO Epoxy Powder E 7100-1 and 4 parts by weight of the same hydrophobic pyrogenic silica used in EXAMPLE 1 was then prepared

by blending the two powders together in a tumbling jar.

5 The resulting mixture was then applied to a similar Q panel at the same rate using the same electrostatic spray gun. After curing in the same manner as the first coated Q panel, the two resulting coated panels were compared with each other.

10 It was found that, although the coating on the second Q panel was not as glossy as the first, the uniformity of the coating thickness was at least as good. Furthermore, whereas the glossy surface of the first Q panel was readily wet by water, the dull matte surface of the second Q panel was very water-repellent or superhydrophobic. The wide difference in this wettability by water is demonstrated by the fact that a drop of water placed on the first panel would not roll or slide off until the panel was tilted to an angle of over 36°, whereas such a drop rolled freely across the second panel when tilted to an angle of only slightly over 1°.

15 Substantially the same results (i.e. the same water-droplet shedding angles) were obtained when Q panels were coated in the same equipment using instead of the above epoxy resin a heat-curable bisphenol modified glycol-fumarate polyester resin sold by Atlas Chemical Company under the trade name 20 ATLAC 382 E (Registered Trade Mark). This resin was ground in a mortar and pestle and sieved to a particle size of less than 125 microns before use and was used as such and after 95 parts of same were shaken together with 5 parts by weight of the same hydrophobic pyrogenic silica for 15 minutes on a Red Devil (Registered Trade Mark) paint shaker.

### EXAMPLE 3

40 The same resinous powder used in EXAMPLE 1 was also used in this Example together with the same fluidized-bed apparatus described therein and its performance alone was compared with the performance of a 45 thoroughly dry blended mixture of 90 parts of same by weight with 10 parts by weight of the same hydrophobic pyrogenic silica used in EXAMPLE 1.

50 Once again it was found that the mixture fluidized more smoothly and evenly than the resinous powder alone. However, since simple flat strips of metal were coated in this Example, little if any difference was noted in the uniformity of the thickness of the deposited coating. However, it was noted, as in 55 EXAMPLE 2, that the coating made with the resinous powder alone was glossier but nowhere near as water-repellant as that formed with the mixture. This was readily seen from the 60 unique silvery sheen which surrounded only the

strip which was coated with the mixture when the two strips were immersed in water as well as from the wide difference in contact angle formed between the said strips and the water, namely about 65° in the case of the strip coated with resin only compared to 135° with the other strip.

It will be seen from the above examples that, while less than 1% of the hydrophobic pyrogenic silica is quite capable of producing dramatic improvements in handling, flowability and stability of powdered resinous solids, considerably greater concentrations appear to be needed to assure the formation of a superhydrophobic or waterproof coating by powder-coating deposition techniques.

### WHAT WE CLAIM IS:—

1. A powdered coating composition comprising a synthetic organic resinous particulate solid below 500 microns in particle size and at least 0.1% by weight thereof of hydrophobic pyrogenic silica below 50 millimicrons in particle size.

2. A composition according to claim 1 comprising resinous particles having a particle size of below 500 microns and greater than one micron, the major component in which is a film-forming synthetic organic polymer and between 0.1% and 25% by weight of said resinous particles of separate particles of a finely divided, hydrophobic pyrogenic silica having an average particle size below 50 millimicrons.

3. A composition as claimed in claim 1 or 2 wherein the surface of the silica has organosilicon groups chemically attached thereon.

4. A composition according to any one of claims 1, 2 or 3 wherein said organosilicon groups conform to the general formula:



where Si is silicon, each R is any alkyl, aryl, alkaryl, alkoxy, aryloxy, alkaryloxy, or aralkoxy radical; a is 2 or 3; each X is a halogen or hydroxyl radical; b is 0 to 1; and the sum of a+b is 3.

5. A composition according to any one of claims 2 to 4 wherein said film-forming synthetic organic polymer is an epoxy resin, a vinyl resin, a nylon, a polyester, or an  $\alpha$ -mono-olefinic hydrocarbon polymer, or copolymers or modified polymers derived from any of these.

6. A composition as claimed in any one of claims 2 to 5 wherein the silica has an average particle size below 20 millimicrons and the weight proportion of said silica to said resinous particles is between 2:98 and 10:90.

7. A composition as claimed in any one of claims 3 to 6 wherein said organosilicon groups

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on said silica amount to at least 1% of the total weight of the silica.

8. A composition as claimed in claim 1 and substantially as described in any one of  
5 examples 1 to 3.

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